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SOLID ELECTROLYTIC FUEL CELL

15 [Abstract]

PURPOSE: To prevent the crack of a solid electrolyte by a thermal distortion by using a seal material in which a specified volume of  $\text{SnO}_2$  particles having a specified particle size are added to a glass having specified values of thermal expansion coefficient and melting point.

20 CONSTITUTION: A seal member 6 is applied to the connecting part between a solid electrolyte 1 and a ceramic tube 3 of different member in a solid electrolytic fuel cell, and the both are sealed and fixed to each other. When a seal member in which 5-40% by volume of  $\text{SnO}_2$  particles having a particle size of 10-500 $\mu\text{m}$  are added to a glass having a melting point of

**800 to 110°C is used as the member 6, the cracking of the solid electrolyte caused by a thermal distortion is prevented.**

**[CLAIMS]**

**[Claim(s)]**

**[Claim 1]** A solid electrolyte fuel cell characterized in that a seal member 6  
5 in which 5 to 40% by volume of  $\text{SnO}_2$  particles having a particle size of 10  
to 500 $\mu\text{m}$  are added to a glass having a thermal expansion coefficient  
more than  $2 \times 10^{-6}/^\circ\text{C}$  higher than that of  $\text{SnO}_2$  particles and a melting point  
of 800 to 110 $^\circ\text{C}$ , is applied to the connecting part between a solid  
electrolyte and a different member and the connecting part is sealed and  
10 fixed.

## **DETAILED DESCRIPTION**

**[Title of the invention]**

### **SOLID ELECTROLYTIC FUEL CELL**

**[Detailed Description of the Invention]**

5   **[0001]**

**[Industrial Application]** This invention relates to a solid electrolyte fuel cell, and particularly to the sealing of the connecting part between a solid electrolyte and a different members of the solid electrolyte fuel cell.

**[0002]**

10   **[Description of the Prior Art]** The solid electrolyte fuel cell shown in FIG. 1 consists of an electrolyte 1, porous electrodes 2 which were applied to both sides of an electrolyte 1, a ceramic tube 3 for supporting the electrolyte 1, an electric ejection line 4 for to supply power, which is connected to the electrode 2, a gas pipe 5 for supplying and discharging  
15   fuel gas to and from the electrolyte 1, a seal member 6 for sealing the fuel gas in a high-temperature section near the electrolyte 1, the rubber plugs 7 sealing the fuel gas in the low-temperature section, the silicone rubber 8, and electric furnaces 9.

**[0003]** In the conventional solid electrolyte fuel cell, the thermal expansion  
20   coefficient of a seal member is similar to that of the electrolyte 1 and the seal member 6 melts at the temperature near the that of the activation of a solid electrolyte fuel cell .

**[0004]**

**[Problem(s) to be Solved by the Invention]** In the conventional solid  
25   electrolyte fuel cell, although the thermal expansion coefficient of a seal

member 6 is similar to that of the electrolyte 1, the crack of the electrolyte 1 has occurred at the time of cooling due to the stress generated by the slight difference of a thermal expansion coefficient, for this reason there was a disadvantage that the fuel gas may be leaked when the temperature is raised, so that the output of a fuel cell may be deteriorated.

[0005] An object of the present invention is to solve the above-mentioned problems in view of the above-mentioned technical level and to provide a solid electrolyte fuel cell without the above disadvantages that the conventional solid electrolyte fuel cell has.

10 [0006]

[Means for Solving the Problem] This invention relates to a solid electrolyte fuel cell characterized in that a seal member 6 in which 5 to 40% by volume of  $\text{SnO}_2$  particles having a particle size of 10 to  $500\mu\text{m}$  are added to a glass having a thermal expansion coefficient more than  $2 \times 10^{-6}/^\circ\text{C}$  higher than that of  $\text{SnO}_2$  particles and a melting point of 800 to  $110^\circ\text{C}$ , is applied to the connecting part between a solid electrolyte and a different member and the connecting part is sealed and fixed.

[0007] As the solid electrolyte used in this invention, generally  $\text{ZrO}_2$  can be used, and as a glass having a thermal expansion coefficient more than  $2 \times 10^{-6}/^\circ\text{C}$  higher than that of  $\text{SnO}_2$  particles and a melting point of 800 to  $110^\circ\text{C}$ , the common glass can be used since it has such a property.

[0008]

[Function] After operating a solid electrolyte fuel cell and raising its temperature up to a high temperature (800 to  $1100^\circ\text{C}$ ), when it descends

to a room temperature, difference of thermal expansion coefficients among those of a sealing material matrix (glass), a dispersed particle ( $\text{SnO}_2$ ) and a solid electrolyte causes a distortion among them. If the sealing material in this invention is used, the crack generated by the distortion which occurs in a sealing material can be prevented from making a solid electrolyte generate distortion.

[0009] The reason to add a seal member of this invention are added to a glass having a thermal expansion coefficient more than  $2 \times 10^{-6}/^\circ\text{C}$  higher than that of  $\text{SnO}_2$  particles (its thermal expansion coefficient:  $4 \times 10^{-6}/^\circ\text{C}$ ) and a melting point of 800 to  $10^\circ$  is to generate a crack in the sealing material and not to generate a crack in the solid electrolyte at the operating temperature (800 to  $1100^\circ\text{C}$ ) of a solid electrolyte fuel cell. In addition,  $\text{SnO}_2$  particles exist in the condition of being dispersed in the glass.

[0010] The sealing material of this invention is not affected under stress by generating a crack in itself so that it prevents generation of the crack in the solid electrolyte. When it is used again, however, a crack is disappeared by being heated and melted so that it can be used as a sealing material again.

[0011] If a sealing material in which  $\text{SnO}_2$  with a mean particle diameter of 20 micrometers is added by 10 capacity % in common glass (thermal expansion coefficient:  $9.6 \times 10^{-6}/^\circ\text{C}$ ) is used in this invention as an example of the sealing materials used in this invention, the flexural strength is about  $2.8 \text{ kgf/cm}^2$ .

[0012] The photograph of the microstructure of the sealing material of this

invention taken by an optical microscope (magnifications: 500 times) is shown in FIG 1.

[0013]

[Example] The experiment on the sealing material used for the solid electrolyte fuel cell of this invention has performed using PbO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> glass as a matrix. The experimental result will be described as follows.

[0014] Effect of the thermal expansion coefficient of a sealing material on a solid electrolyte (8mol% Y<sub>2</sub>O<sub>3</sub>ZrO<sub>2</sub>) (Table 1)

The sealing material in which SnO<sub>2</sub> with mean particle diameter of 30 micrometers and thermal expansion coefficient of  $4 \times 10^{-6}/^{\circ}\text{C}$  is dispersed by 20 capacity % in the sealing material matrix having thermal expansion coefficient of  $4 \times 10^{-6}/^{\circ}\text{C}$ ,  $6 \times 10^{-6}/^{\circ}\text{C}$ , and  $8 \times 10^{-6}/^{\circ}\text{C}$  respectively is applied as a sealing material of FIG. 1. After checking the leakage of the sealing at 1000°C, descending a temperature and drawing the solid electrolyte out off the furnace and observed if the crack had occurred or not. Subsequently put it back to the furnace and raise temperature and checke the sealing at 1000°C again. This result is shown in Table 1.

[Table 1]

Thermal expansion coefficient of a sealing material	$4 \times 10^{-6}/^{\circ}\text{C}$	$6 \times 10^{-6}/^{\circ}\text{C}$	$8 \times 10^{-6}/^{\circ}\text{C}$
Thermal expansion coefficient of a sealing material - Thermal expansion coefficient of a dispersed particle	○	$2 \times 10^{-6}/^{\circ}\text{C}$	$4 \times 10^{-6}/^{\circ}\text{C}$
Sealing at a high temperature	○	○	○

Sealing after descending temperature	Crack was found in the solid electrolyte	Crack was found in the sealing material	Crack was found in the sealing material
Sealing after re-raising temperature	X	o	o
Overall assessment	X	o	o

[0015] From the above result, we founded that a crack does not occur in a solid electrolyte when the thermal expansion coefficient of a sealing material matrix is large, and a difference of the thermal expansion coefficient of the sealing material matrix and a dispersed particle material is more than  $2 \times 10^{-6}/^{\circ}\text{C}$ .

[0016] Effect of the diameter of the particles dispersed in the sealing material with the generation of the crack in a solid electrolyte (Table 2)

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15 The sealing material in which  $\text{SnO}_2$  with mean particle diameter of 5, 10, 30, 250, 500, and 750 micrometers and thermal expansion coefficient of  $4 \times 10^{-6}/^{\circ}\text{C}$  is dispersed by 20 capacity % in the sealing material matrix having thermal expansion coefficient of  $8 \times 10^{-6}/^{\circ}\text{C}$  respectively is applied as a sealing material of FIG. 1. After checking the leakage of the sealing at



1000°C, the temperature was lowered and the solid electrolyte was drawn out of the furnace and was observed if the crack had occurred or not. Subsequently, the electrolyte was put back into the furnace and temperature was raised before checking the sealing at 1000°C again. This

5 result is shown in Table 2.

[Table 2]

Particle diameter	5	10	30	250	500	750
Sealing at a high temperature	○	○	○	○	○	X
Sealing after descending a temperature	Crack was found in the solid electrolyte	Crack was found in the sealing material	←	←	←	←
Sealing after re-raising a temperature	X	○	○	○	○	X
Overall assessment	X	○	○	○	○	X

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[0017] The above result shows that a crack does not occur in a solid electrolyte, if the diameter of a particulate material is 10 to 500 micrometers.

[0018] Effect of the amount of the dispersed particle mixed in a sealing

material on the generation of crack in a solid electrolyte (Table 3)

The sealing material in which  $\text{SnO}_2$  with mean particle diameter of 30 micrometers and thermal expansion coefficient of  $4 \times 10^{-6}/^\circ\text{C}$  is dispersed by 3, 5, 10, 20, 40, and 60 capacity % in the sealing material matrix having thermal expansion coefficient of  $8 \times 10^{-6}/^\circ\text{C}$  respectively is applied as a sealing material of FIG. 1. After checking the leakage of the sealing at  $1000^\circ\text{C}$ , the temperature was lowered and the solid electrolyte was removed from the furnace and was observed if the crack had occurred or not. Subsequently, the electrolyte was put back into the furnace and the temperature was raised before checking the sealing at  $1000^\circ\text{C}$  again. This result is shown in Table 2.

[Table 3]

amount of the dispersed particle	3	5	10	20	40	60
Sealing at a high temperature	○	○	○	○	○	X
Sealing after descending a temperature	Crack was found in the solid electrolyte	Crack was found in the sealing material	←	←	←	←
Sealing after re-raising a	X	○	○	○	○	X

temperatur e						
Overall assessmen t	X	o	o	o	o	X

[0019] The above result shows that a crack does not occur in a solid electrolyte, if the amount of dispersed particle is 5 to 40 capacity %.

[0020]

- 5 [Effect of the Invention] This invention provides a solid electrolyte fuel cell which can prevent the generation of a crack in a solid electrolyte caused by the thermal strain that is generated by the difference of thermal expansion coefficients among those of a sealing material, a dispersed particle and a solid electrolyte causes a distortion among them at the time
- 10 of raising and descending temperature.

[Brief Description of the Drawings]

FIG.1 is an explanatory view of a solid electrolyte fuel cell.

- FIG. 2 is an optical microscope photograph in which the detailed
- 15 organization of the sealing material used by this invention is shown.